X-ray Diffuse Scattering

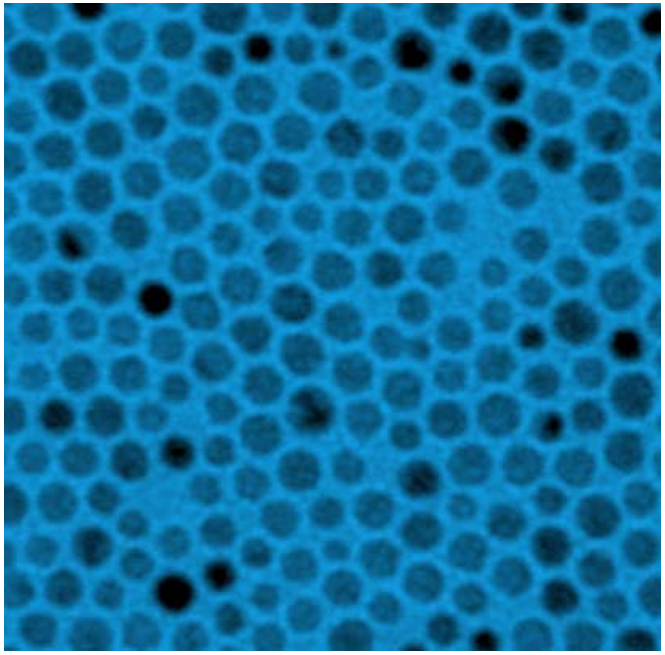


Figure 1: TEM image of self-assembled monolayer of Au nanoparticles (6 nm diameter). Image is 100 nm by 100 nm.

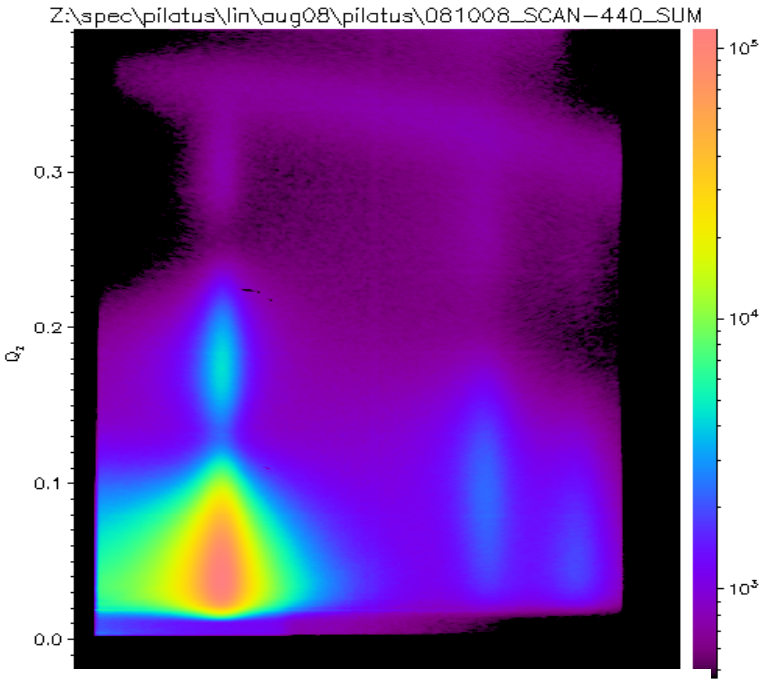
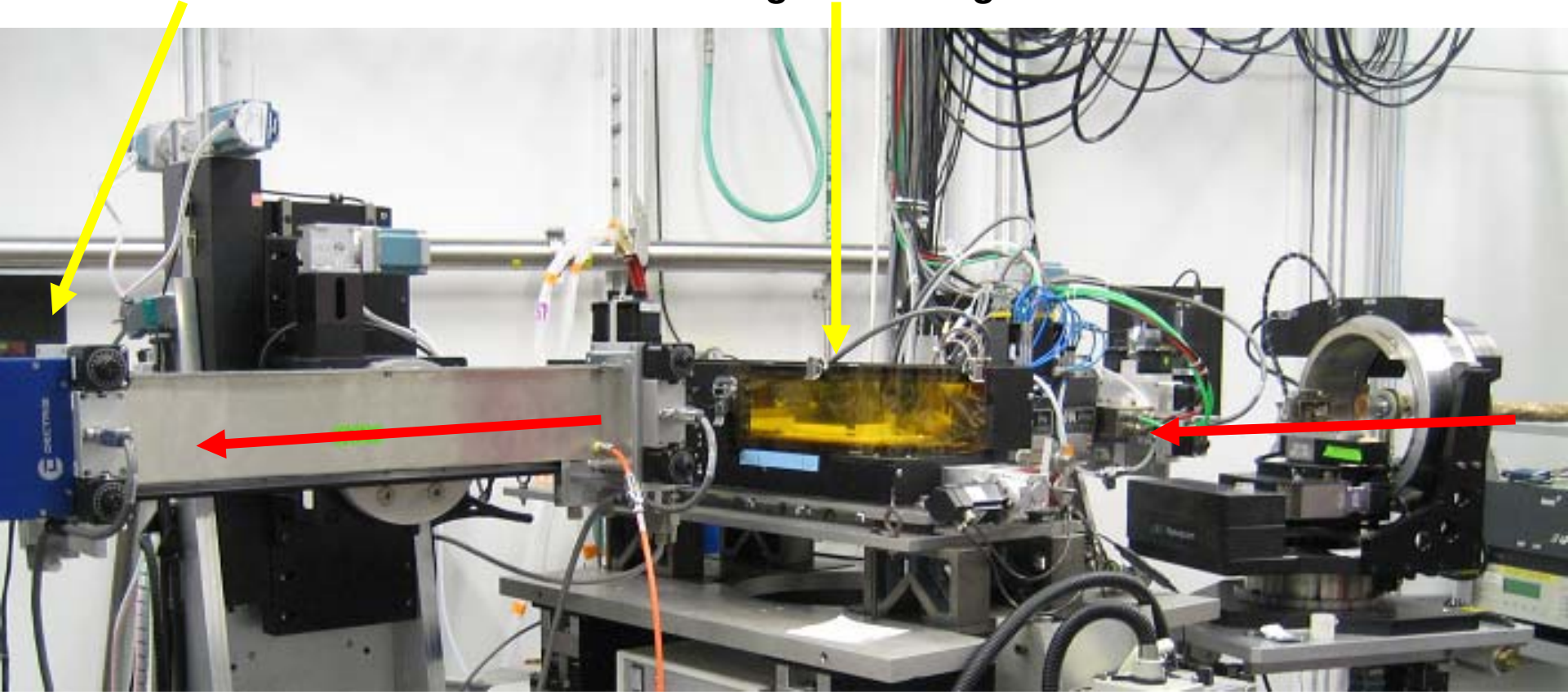


Figure 2: 2D image of the Au-nanoparticles monolayer filmscattering pattern collected by Pilatus detector

Experiment Setup

Argonne,APS Sector 15



PILATUS detector
(**pi**xel appar**atu**s for the **S**LS)

Two-dimensional hybrid pixel array

A hybrid pixel comprises a preamplifier,
a comparator and a counter.

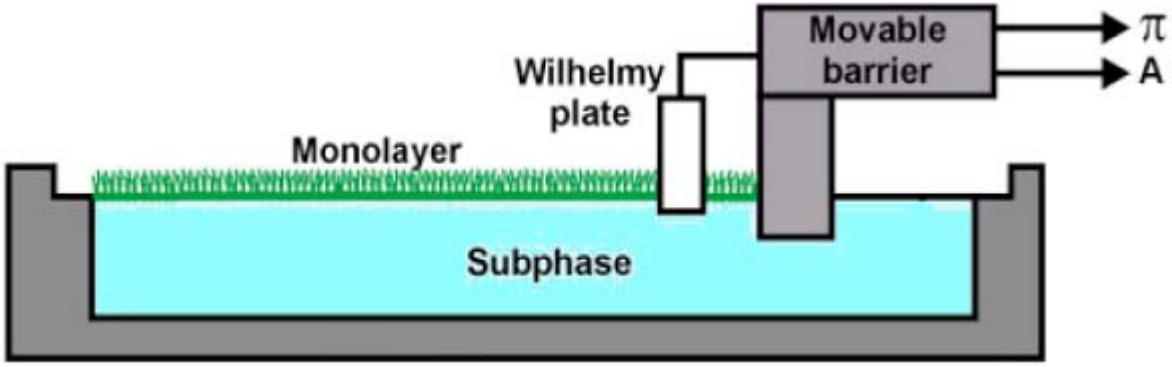
Advantage: no readout noise
high signal-to-noise ratio
small read-out time …

	Integrating Detector	PILATUS Detector
Principle	Charge is accumulated and then converted.	X-ray is counted above certain threshold.
Count Rate Dynamic Range	Unlimited	Limited to ~1.5 MHz/pixel/s
Detective Quantum Efficiency	80%@8 - 12 keV	100%@8 keV, 80%@12 keV, 50%@16 keV
Dynamic Range	32'768 - 131'072	1'048'576
Framing Rate	0.01 - 0.5 Hz	10 - 100 Hz
Pixel Size	0.05 - 0.15 mm	0.172 mm
Read-out Time	1 - 120 s	5 ms
Signal to Noise Ratio	Limited by dark current and noise	Fluorscent background suppression
Point Spread Function	Several pixels	One Pixel

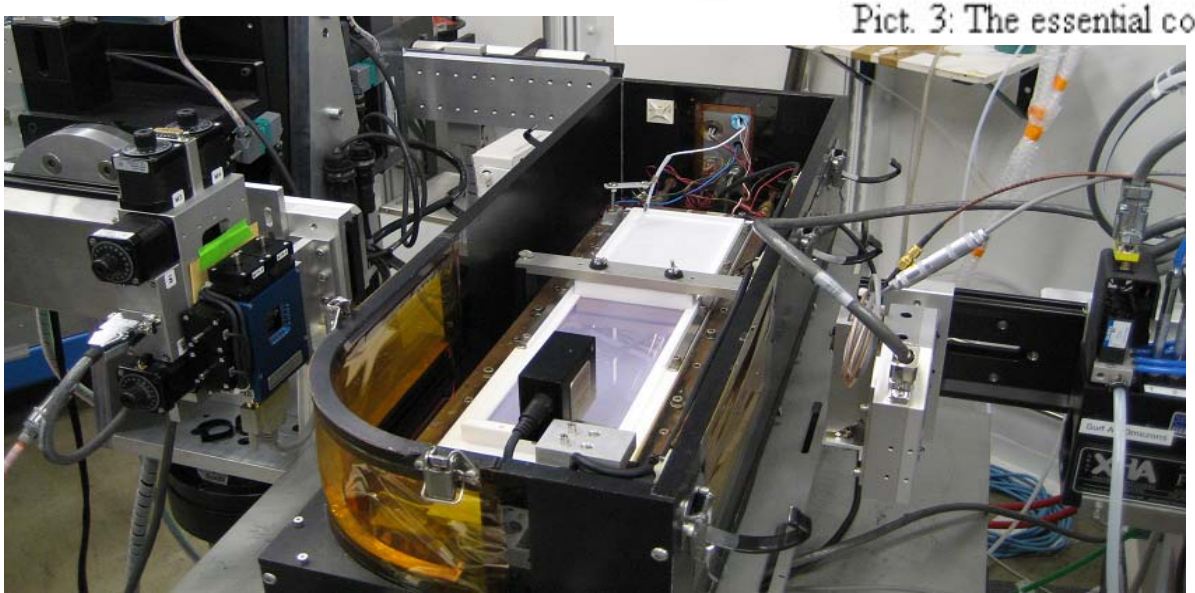
Comparison between integrating detectors and PILATUS detectors

Langmuir Trough

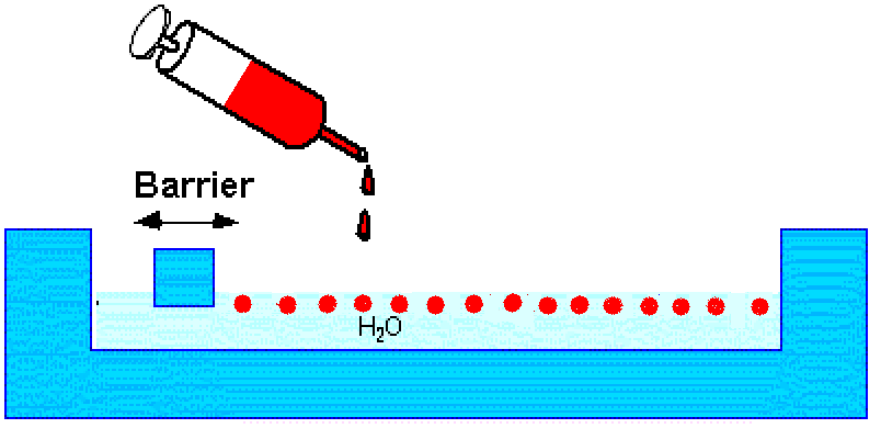
a device for studying the properties of monolayers at an air/water interface

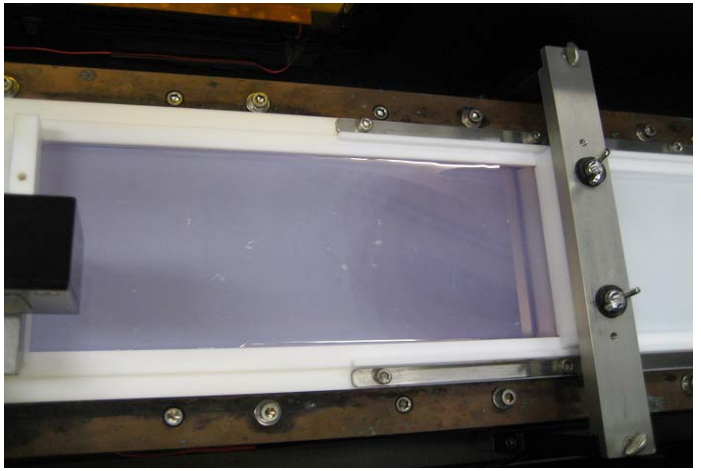


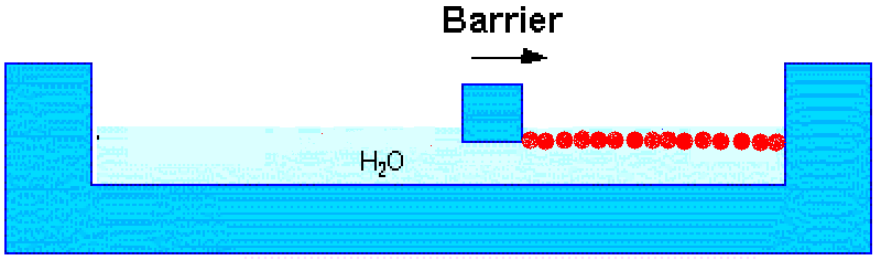
Pict. 3: The essential components of a Langmuir trough

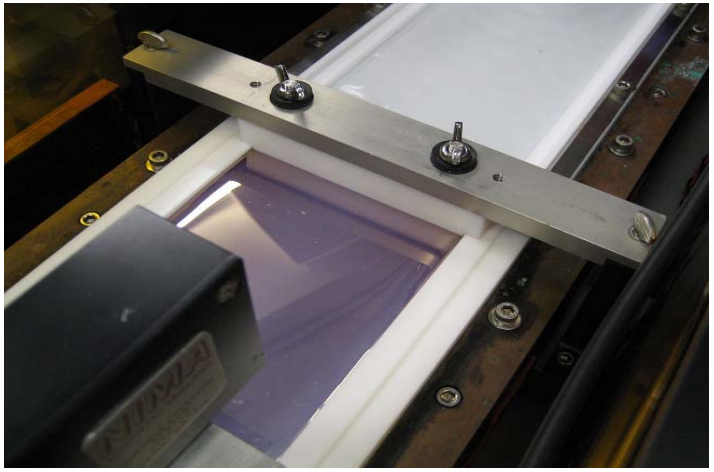


Produce a monolayer

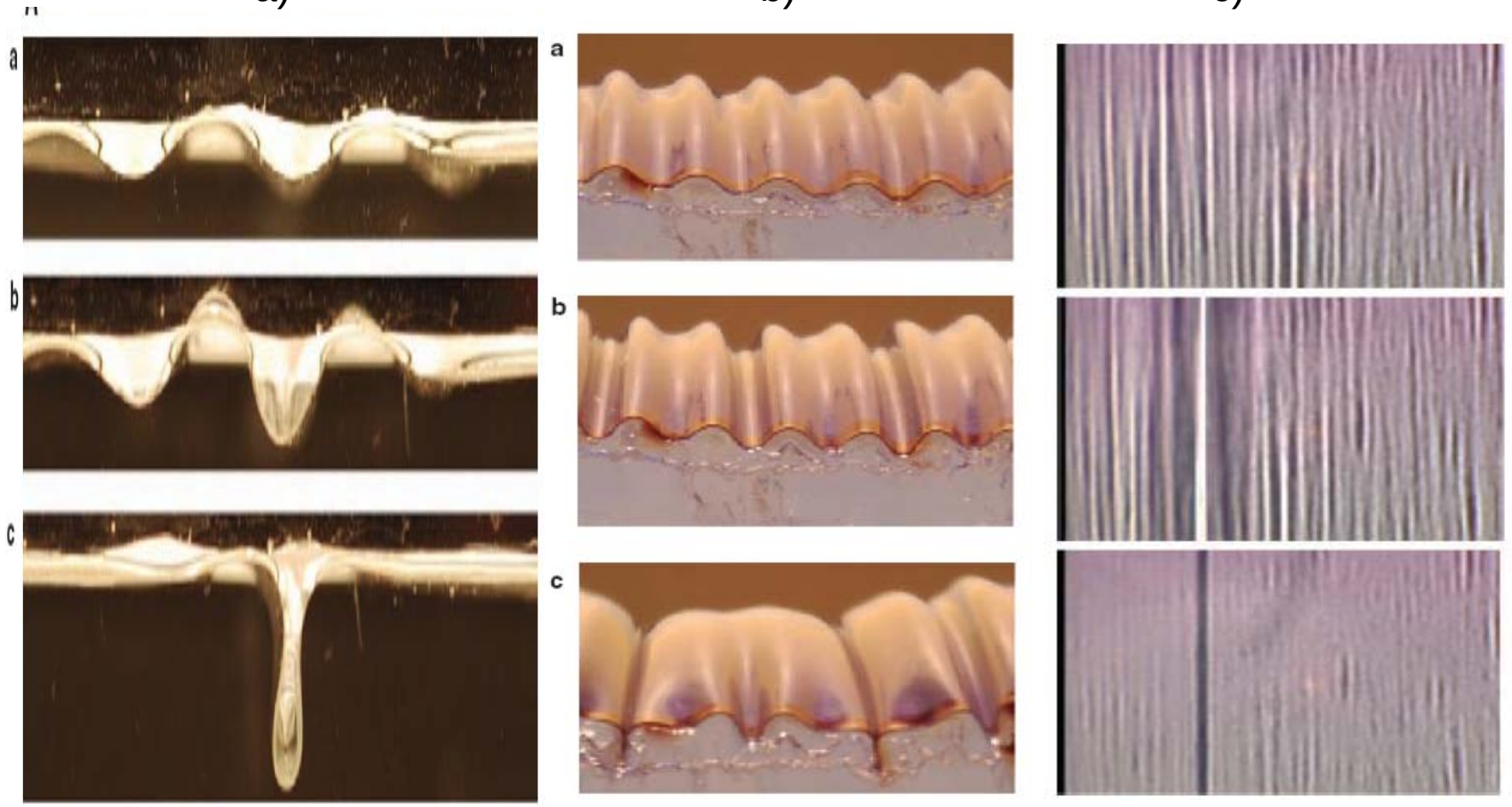








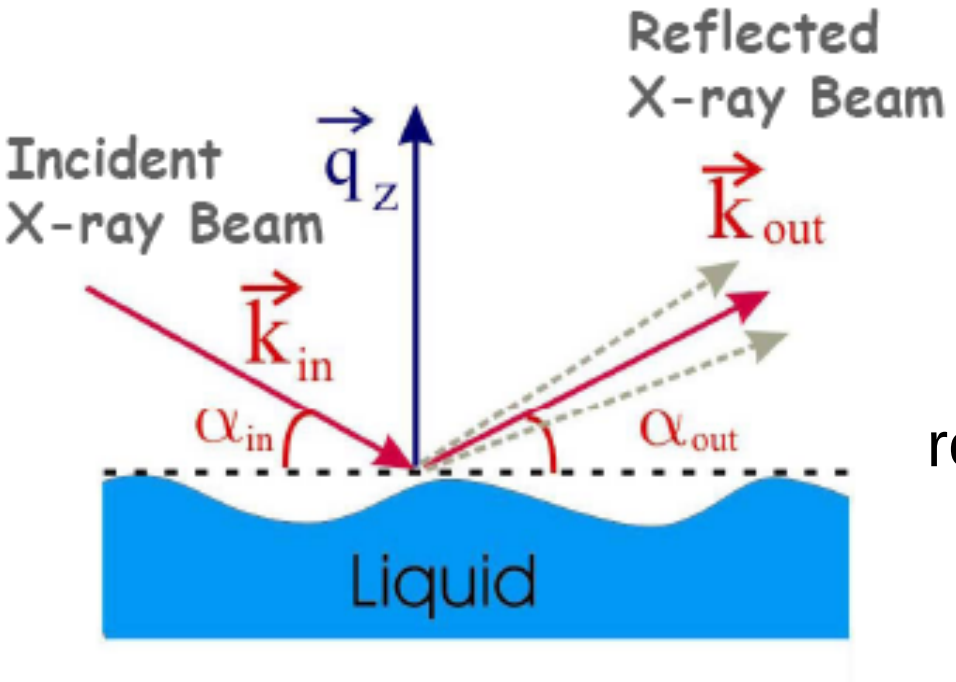
a) b) c)



a)polyester film on water ,imaged from side ,10 μ m thick, λ ~1.6cm
b) polyester film on gel substract ,imaged from side, 10 μ m thick, λ ~3mm
c)trilayer of Au nanoparticles on water ,microscopically imaged from above
15 nm thick, λ ~ 10 μ m
transitioning from uniform wrinkled state to localized folded state

Luka Pocivavsek,Robert Dellsy, *Science* 320, 912 (2008)

Off-specular X-ray diffuse scattering: a probe of surface capillary fluctuation



$$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$$

wave vector transfer

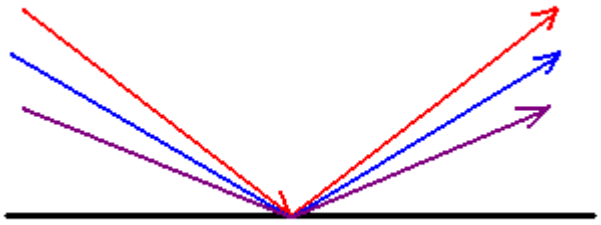
$$q_{xy} = \frac{2\pi}{\lambda}(\cos\alpha_{in} - \cos\alpha_{out})$$

$$q_z = \frac{2\pi}{\lambda}(\sin\alpha_{in} + \sin\alpha_{out})$$

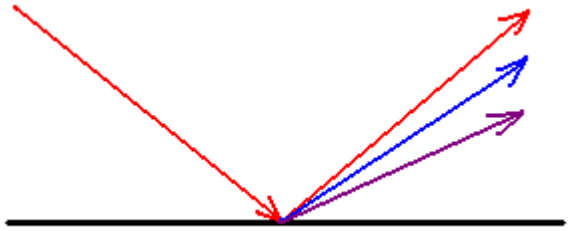
reflectivity ⇒ density profile

diffuse ⇒ surface profile (fluctuating mode)

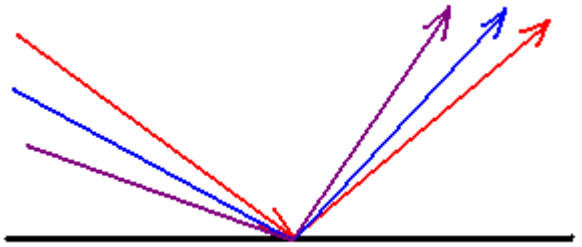
X-ray Scattering Measuring Modes



reflectivity,Qxy=0

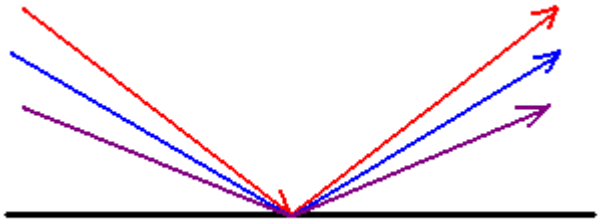


diffuse β scan,
Qz≠0, Qxy ≠0

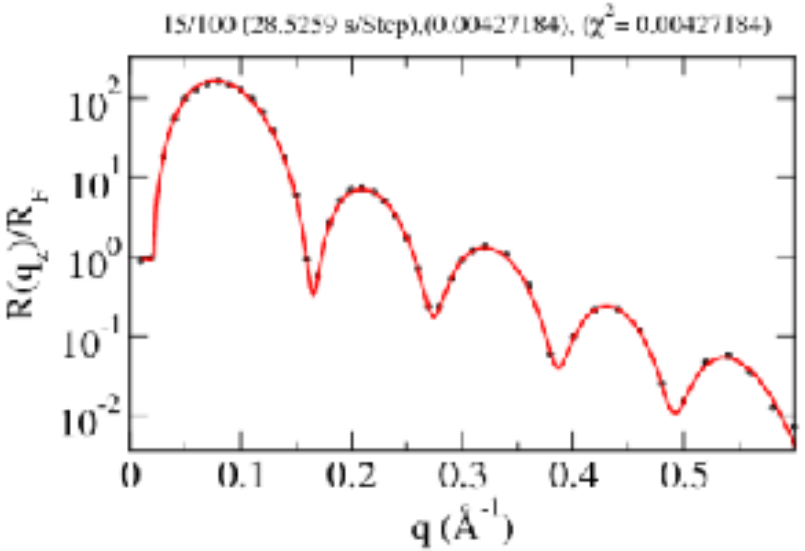


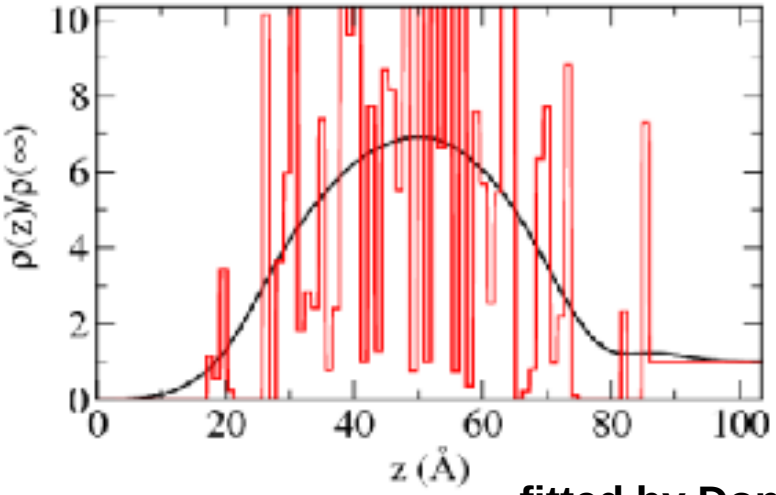
diffuse K scan,
Qz=const, Qxy ≠0

Au monolayer reflectivity example



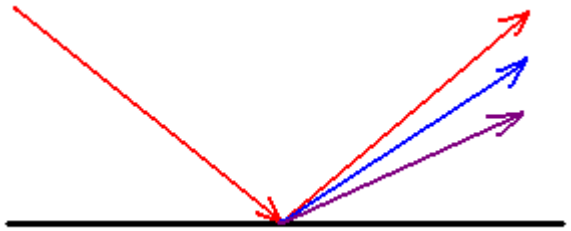
reflectivity,Qxy=0



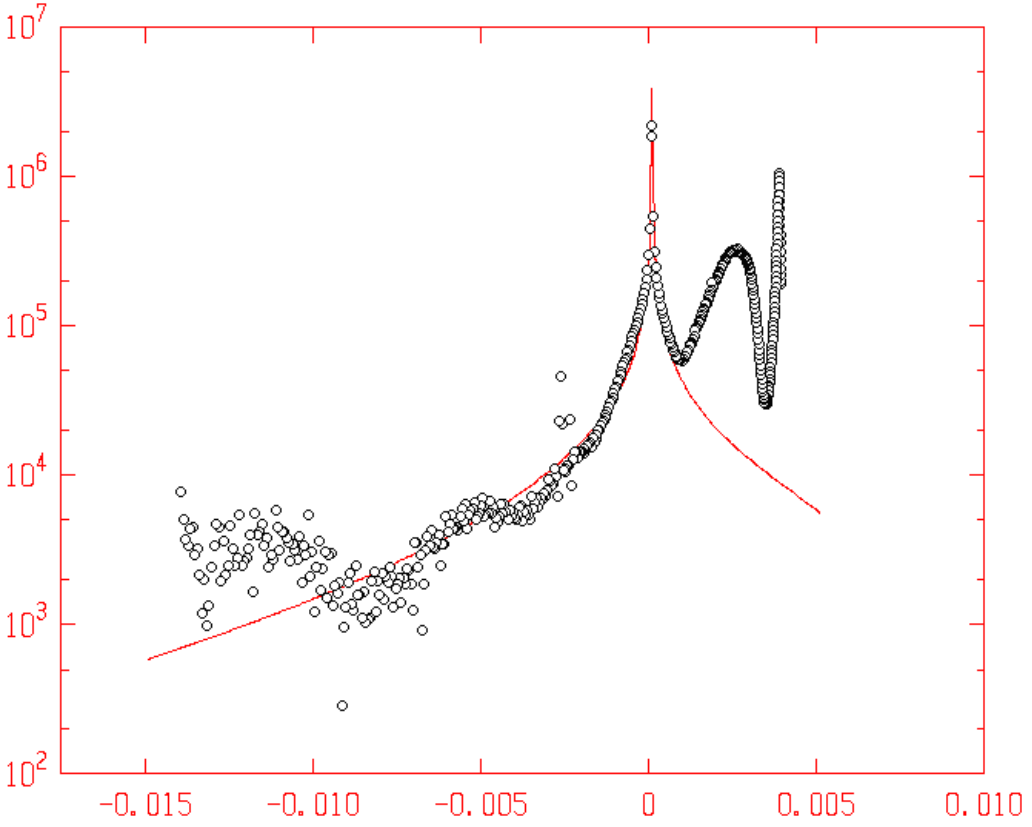


fitted by Dongxu Li

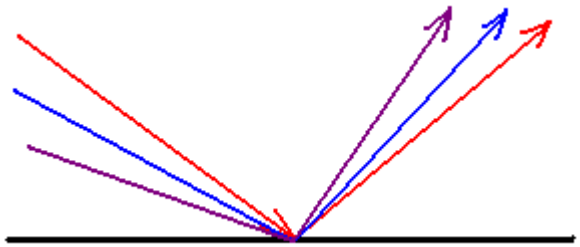
diffuse scattering β scan example



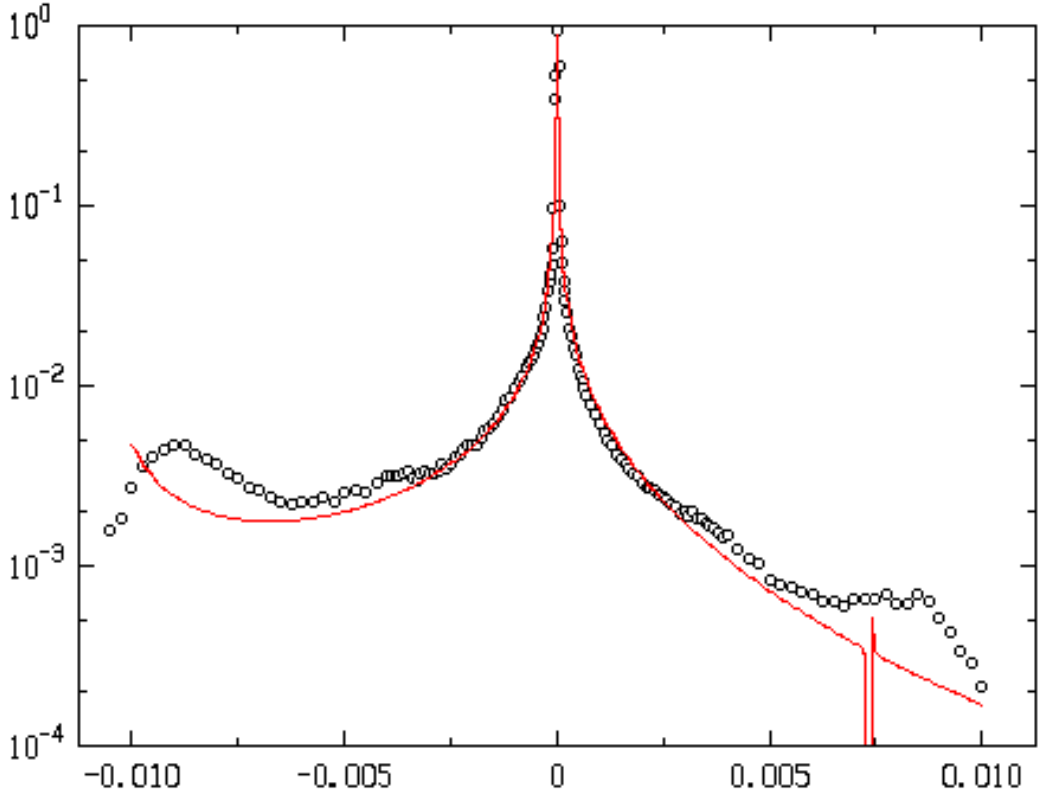
diffuse β scan,
Qz≠0, Qxy ≠0



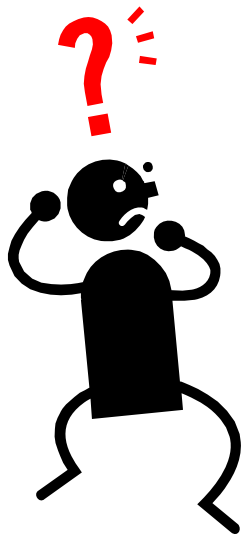
diffuse scattering K scan example



diffuse K scan,
Qz=const, Qxy $\neq 0$



Problems :



Need to figure out!

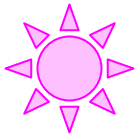
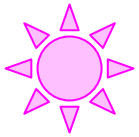
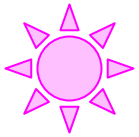
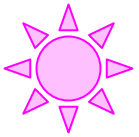
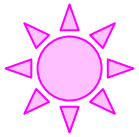
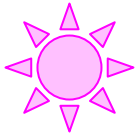
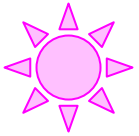
- Uniformity & reproducibility of the sample
- Change in footprint
- Absorption and beam damage
- Multiple scattering?
- Yoneda wings (effect at critical angle)
- Which rule to follow?

long long way to go……

Thanks!

What we have now:

Data:

	XR	GID	Kscan
water			
Au monolayer			
Au multilayer			

Theory:
Born Approximation model , Parratt's theory ,
Sinha's theory (including calculation for Yoneda wings)

The rule we and our codes followed:

Scattering cross-section:

$$\frac{d\sigma}{d\Omega} = \frac{A_0}{\sin^2\alpha}\left(\frac{q_c}{2}\right)^4 \frac{1}{8\pi q_z^2}\left|\Phi(q_z)\right|^2 \left(\frac{1}{q_{\max}}\right)^{\eta} \frac{\eta}{q_{xy}^{2-\eta}}$$

Experimental measured intensity:

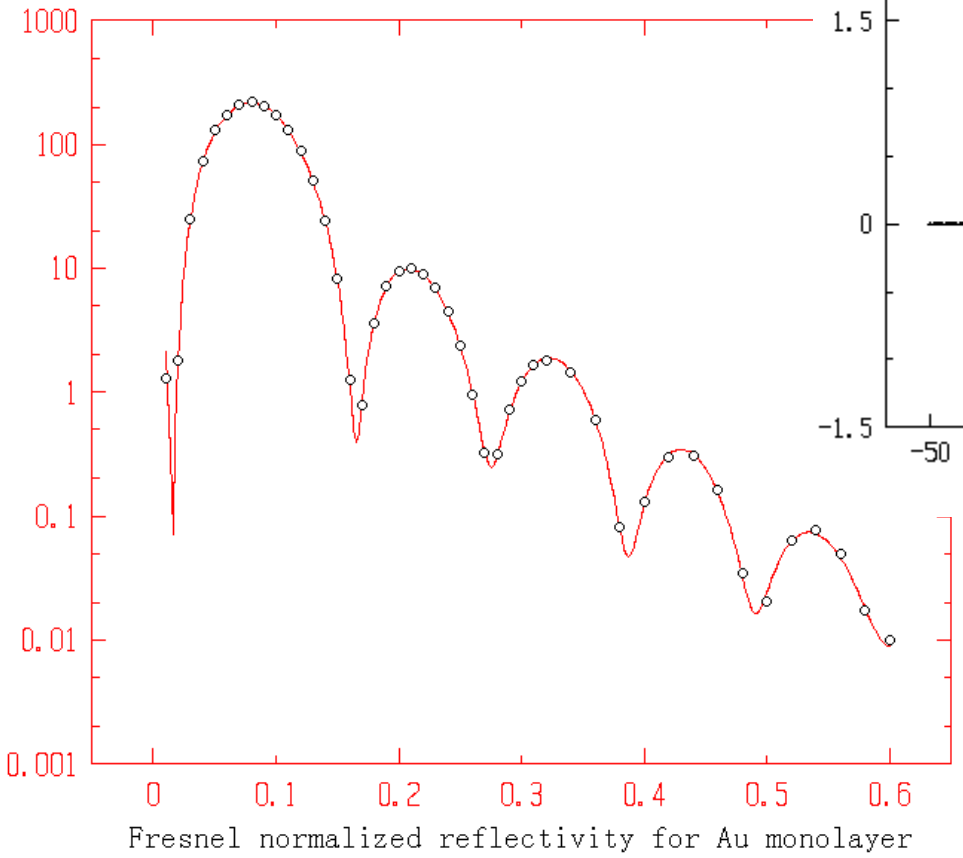
Depends on surface tension γ !

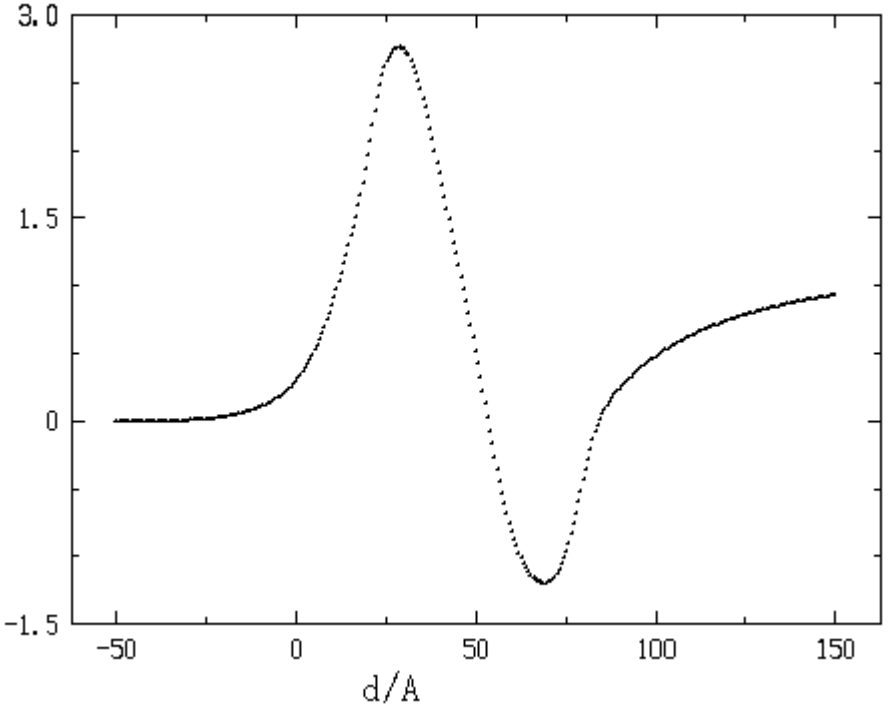
$$I = R_F(q_z)\left|\Phi(q_z)\right|^2 \int_{res} \left(\frac{1}{q_{\max}}\right)^{\eta} \frac{\eta}{q_{xy}^{2-\eta}} dq_x dq_y$$

Constant for K-scan! (constant qz)

Resolution function is very important!

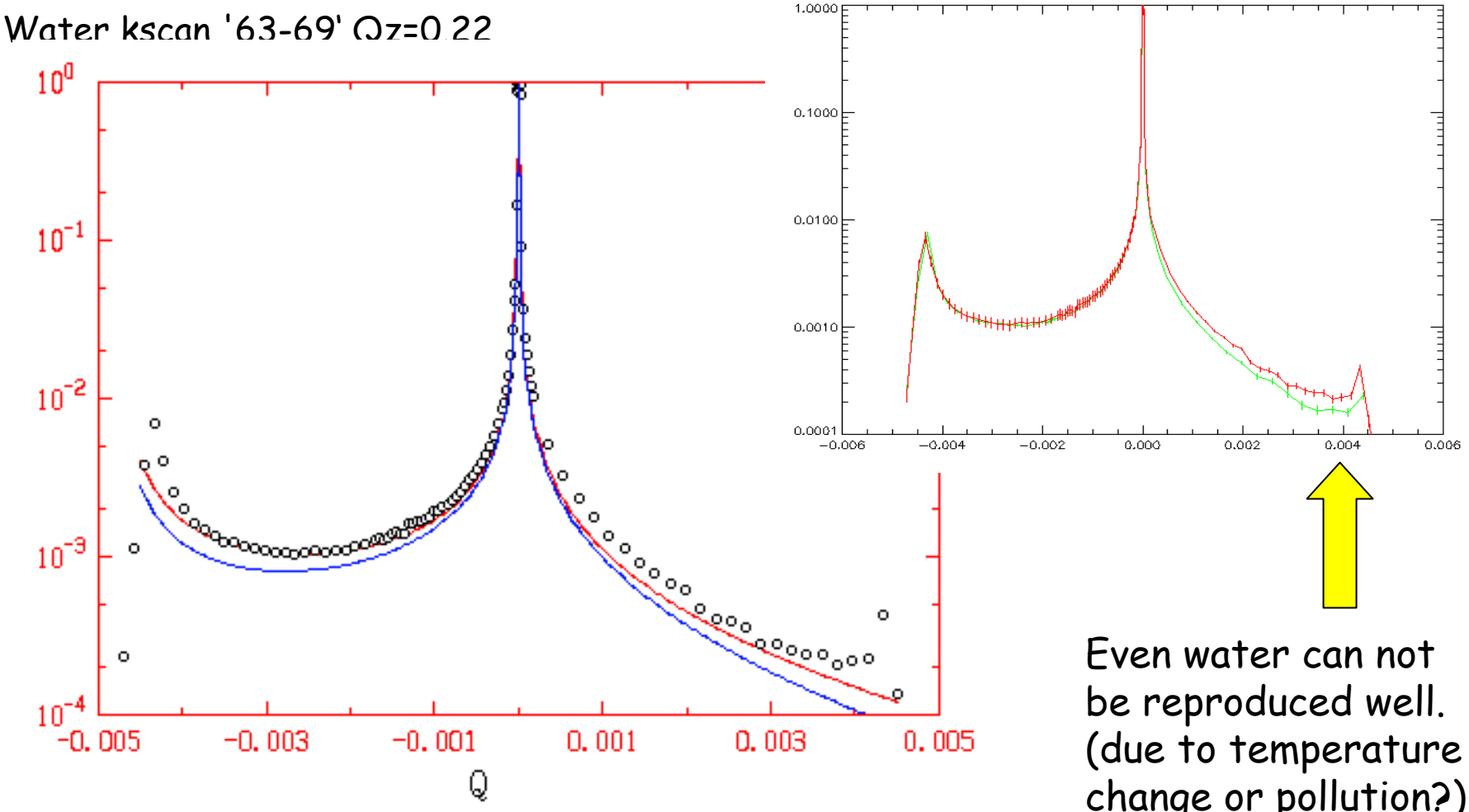
Au monolayer reflectivity fitting





With our fitting code,we're able to fit the reflectivity very well even for Au multilayer,but always get negative density part due to the broadening of error functions.

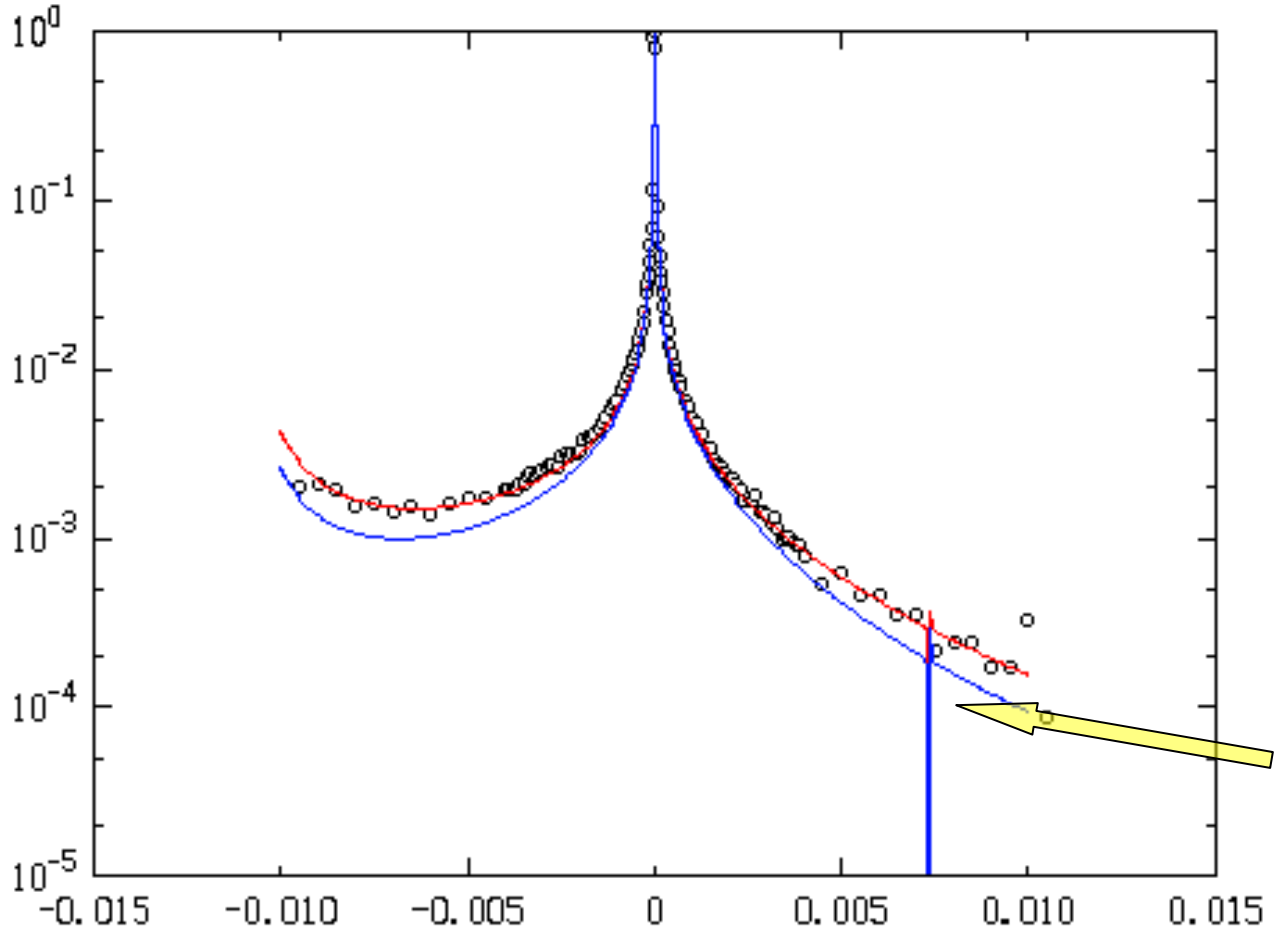
Resolution function calculated from slits size needs to be corrected?



Even water can not be reproduced well. (due to temperature change or pollution?)

Fitting resolution function(fixed γ =72 mN/m):
Blue – fixed Vert. Slit(0.52mm),Hori. Slit(1.89mm) (sli=[11,3])
Red – fitted Vert. Slit(0.53mm),Hori. Slit(3.59mm)

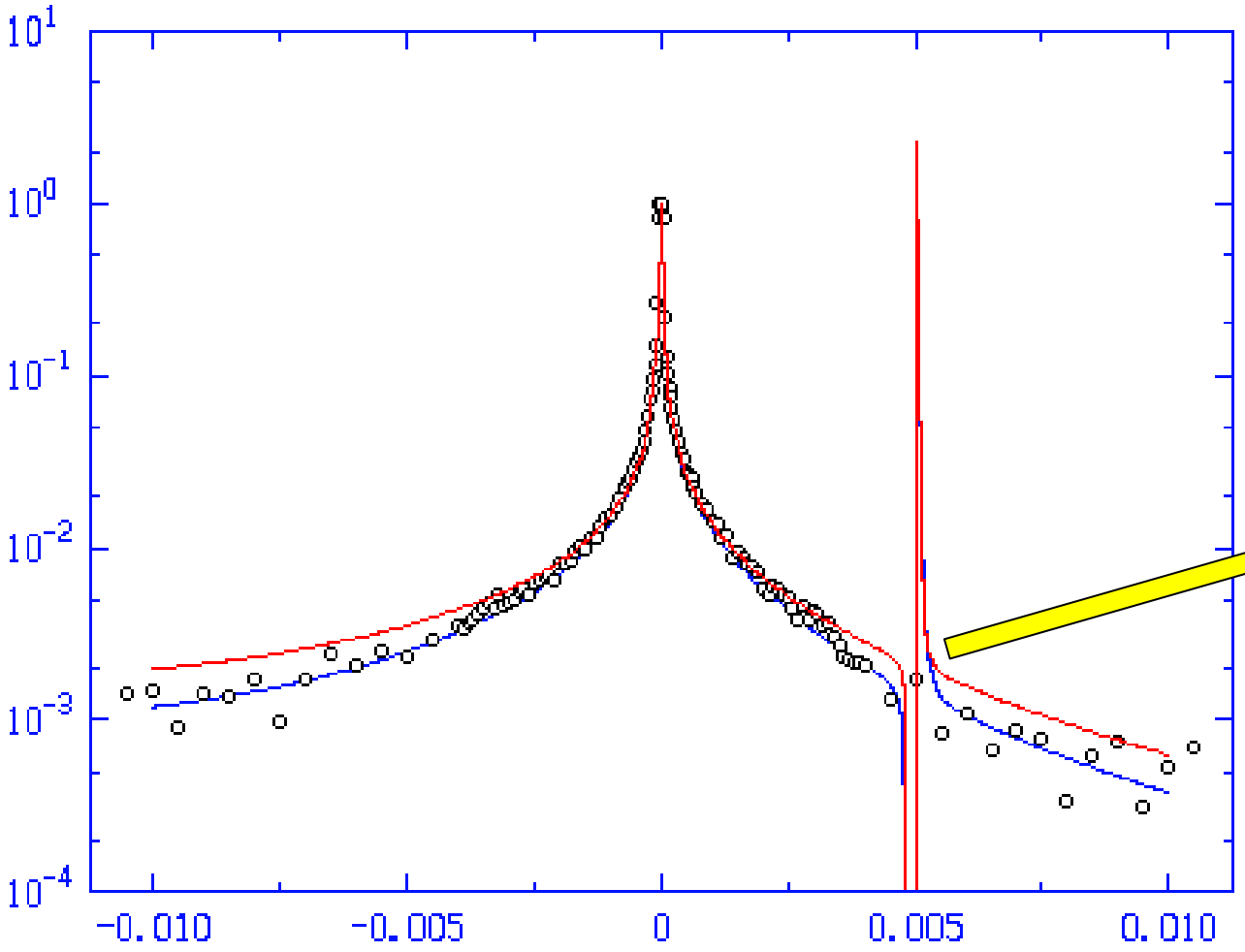
Water '71-77', sli=[11,3],bac=0.5 ,Qz=0.33

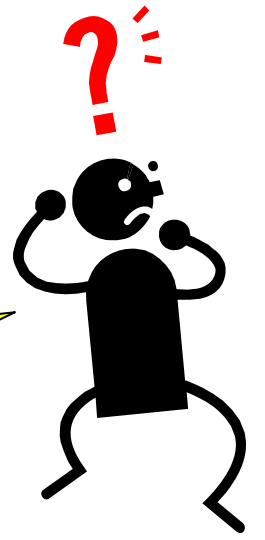


Unknown peak presents at Q~0.073, The position doesn't change with γ.

Fitting resolution function:
Blue – fixed Vert. Slit(0.52mm),Hori. Slit(1.89mm)
Red – fitted Vert. Slit(0.52mm),Hori. Slit(3.61mm)

Water '79-106', sli=[11,3],bac=0.5 ,Qz=0.44





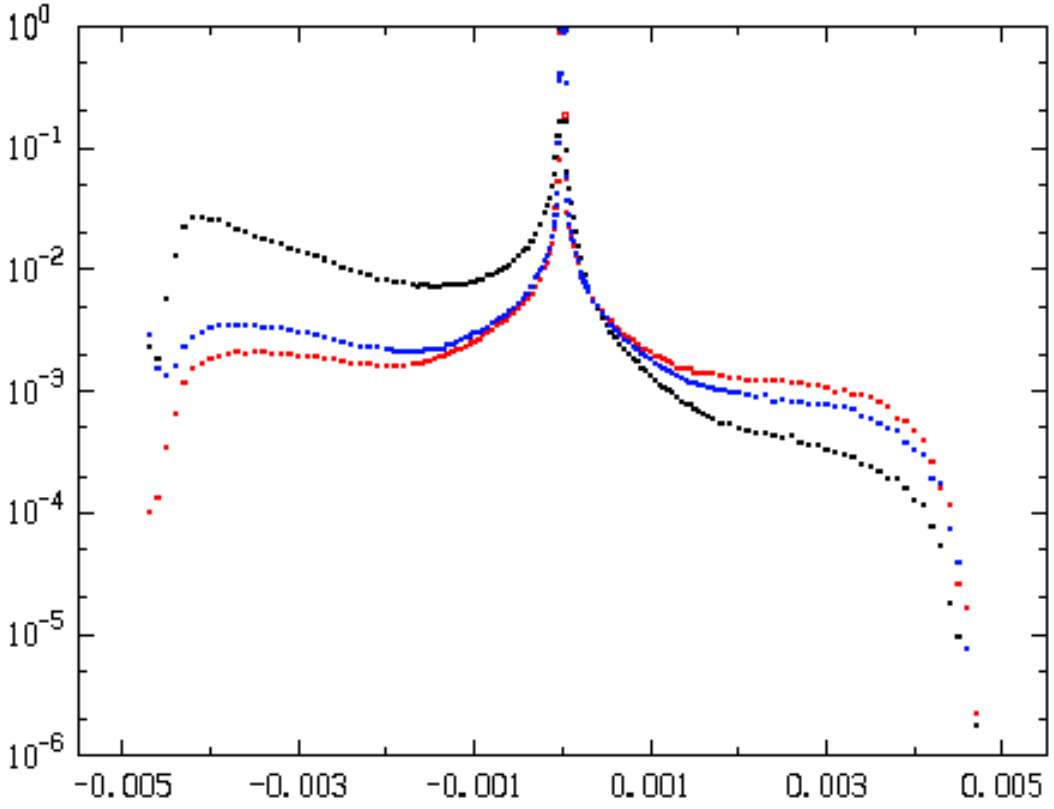
Need to figure out!

The slit size Vert.=0.52 Hori.=1.89 could fit the data perfectly.No cerrection to resolution function.And slit(0.52,3.60) seems also work not bad.

Do we need to correct our resolution function from slit (0.52,1.89) to slit (0.52,3.6)?

Reason?

Big problem:
Ununiformity of sample (beam damage?)
& Lack of reproducibility

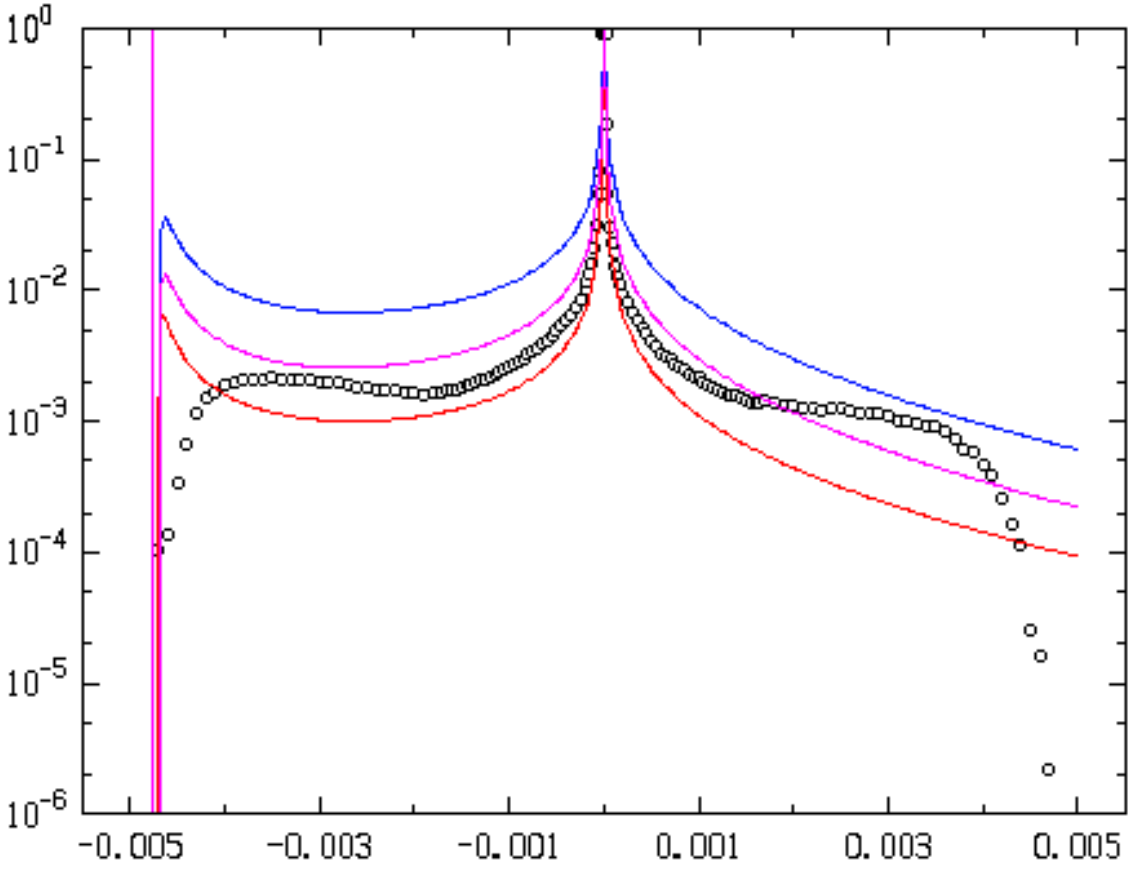


Three data sets for Qz=0.22 are different from each other – monolayer is not reproducible…

black—148(w/thoils),
red—217
blue- 273

Surface tension rules!

monoAu '217-' , sli=[11,3],bac=0.5 ,Qz=0.22

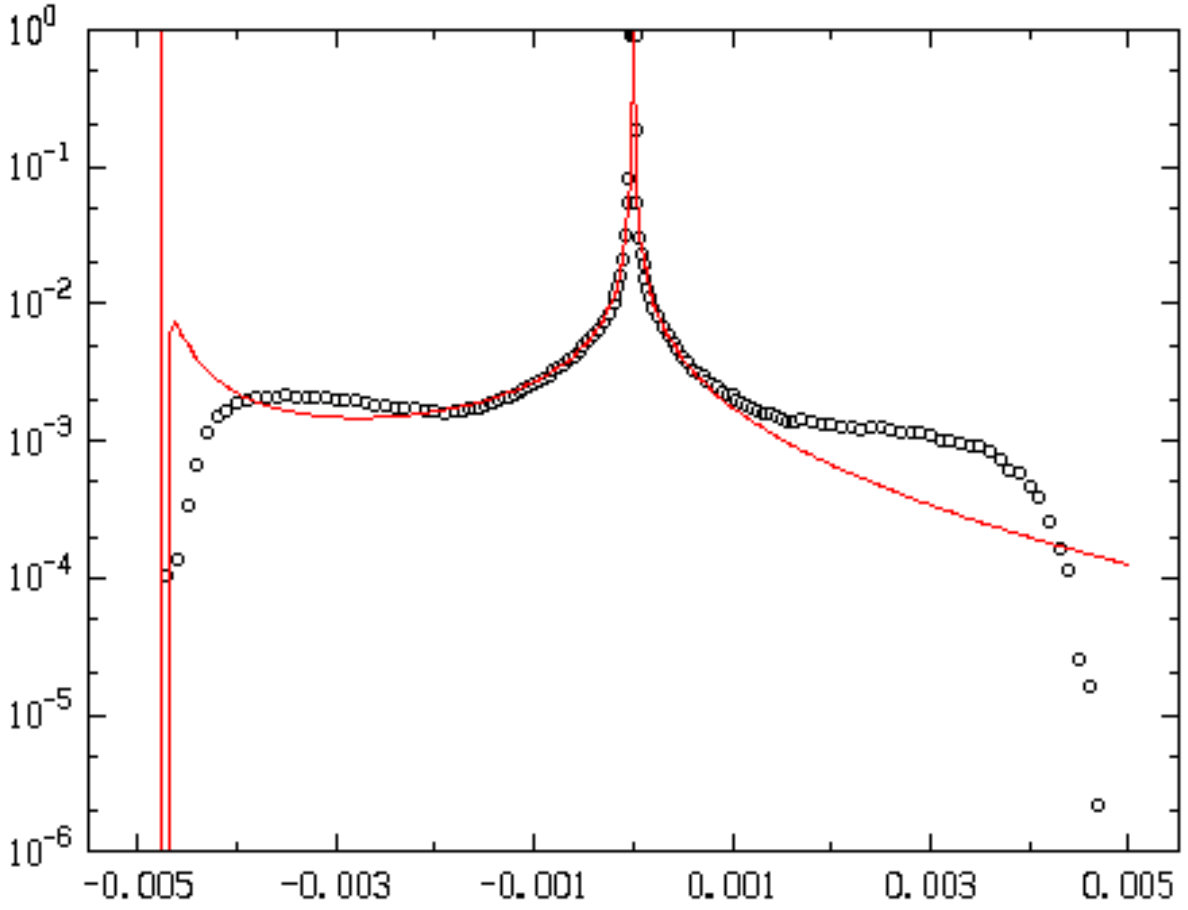


Highly depends on surface tension η

blue-- η =18 (~heptane) magenta-- η =30 red-- η =72(water)

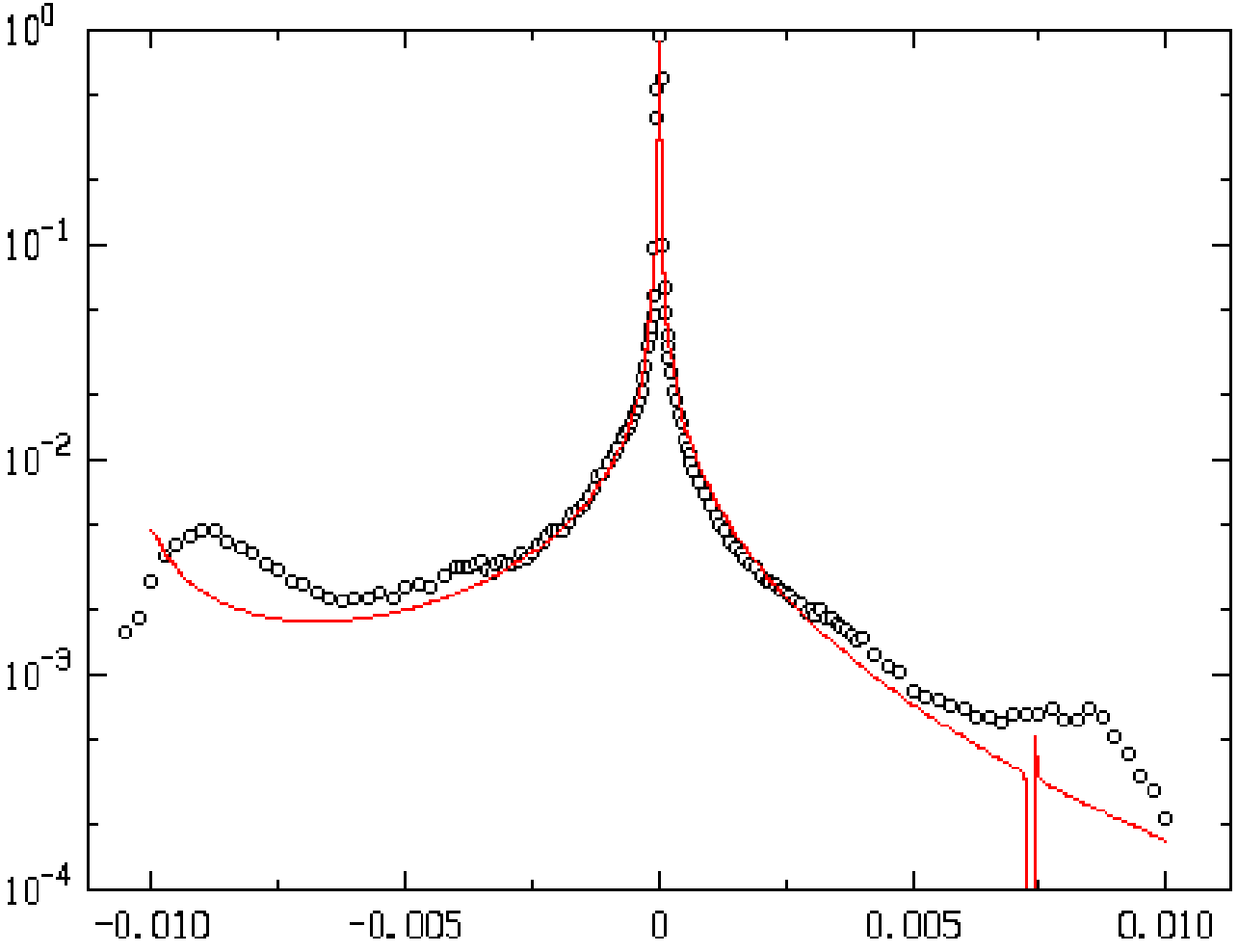
Surface tension fitting
(with fixed slit0.52,1,89)

monoAu '217-', sli=[11,3],bac=0.5 ,Qz=0.22



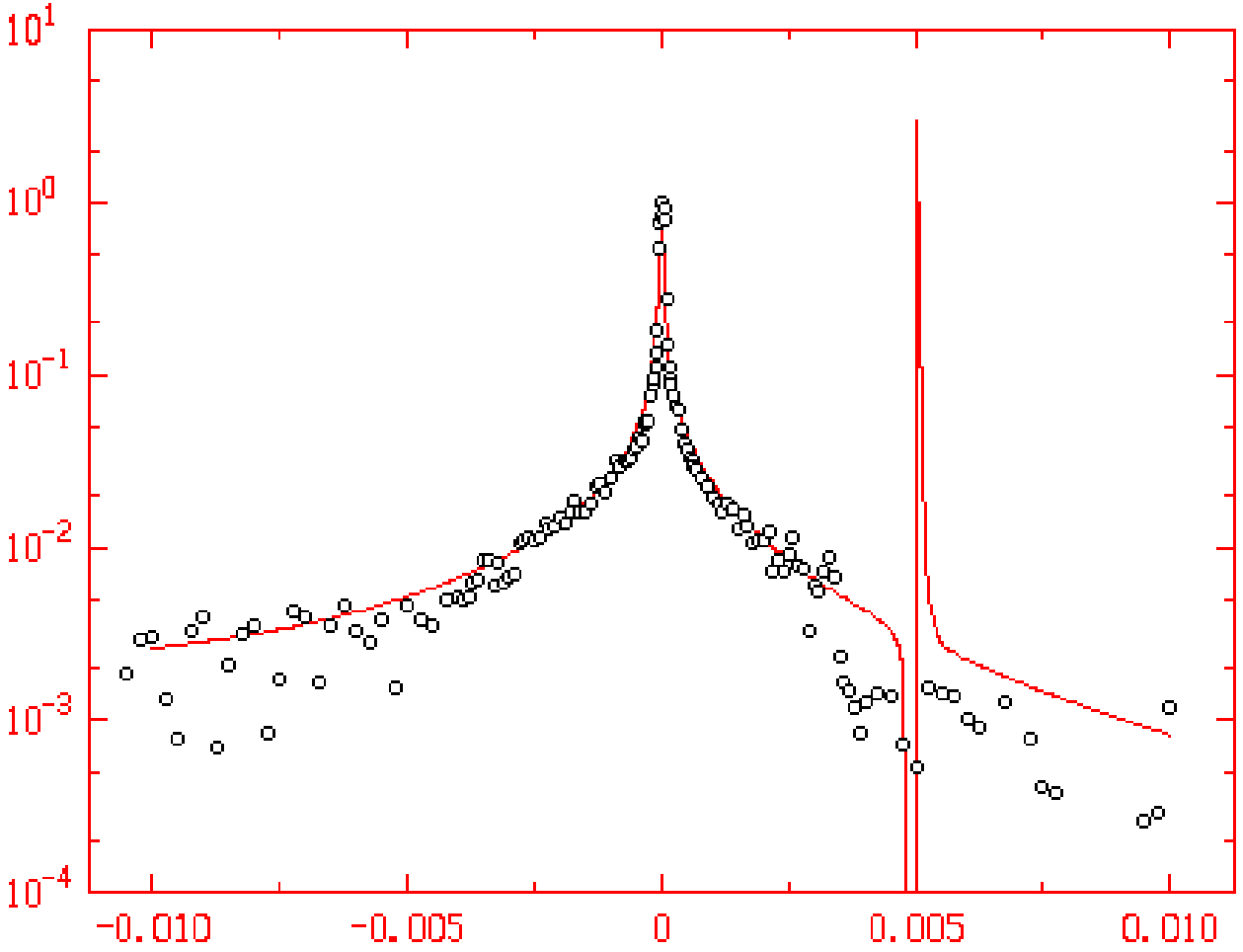
fitted η =45 mN/m (between water 72 & Heptane ~20)

monoAu '313-', sli=[11,3],bac=0.5 ,Qz=0.33

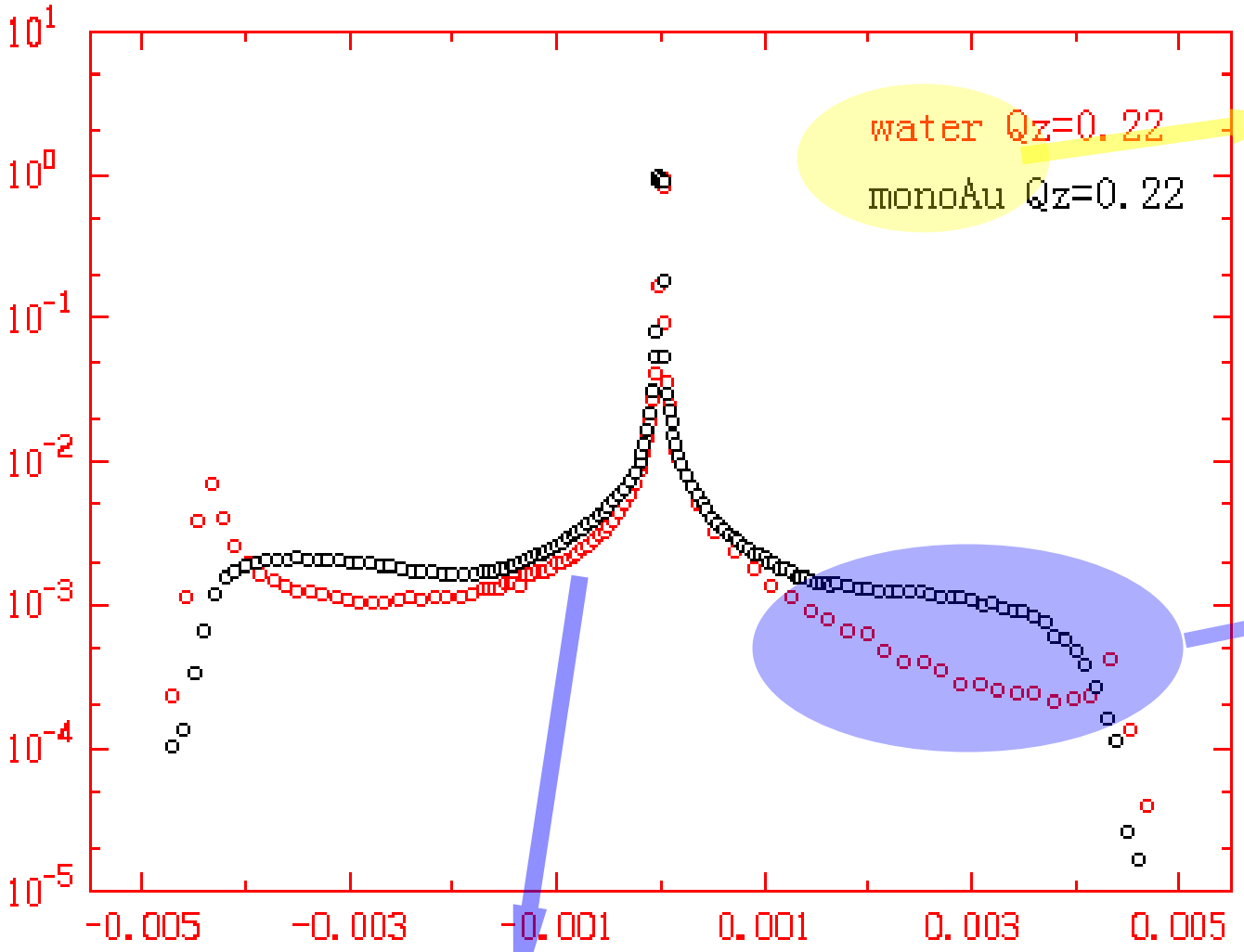


fitted η =45 mN/m

monoAu '299-', sli=[11,3],bac=0.5 ,Qz=0.44



fitted η =48 mN/m



Can we make samples more uniform and reproducible?

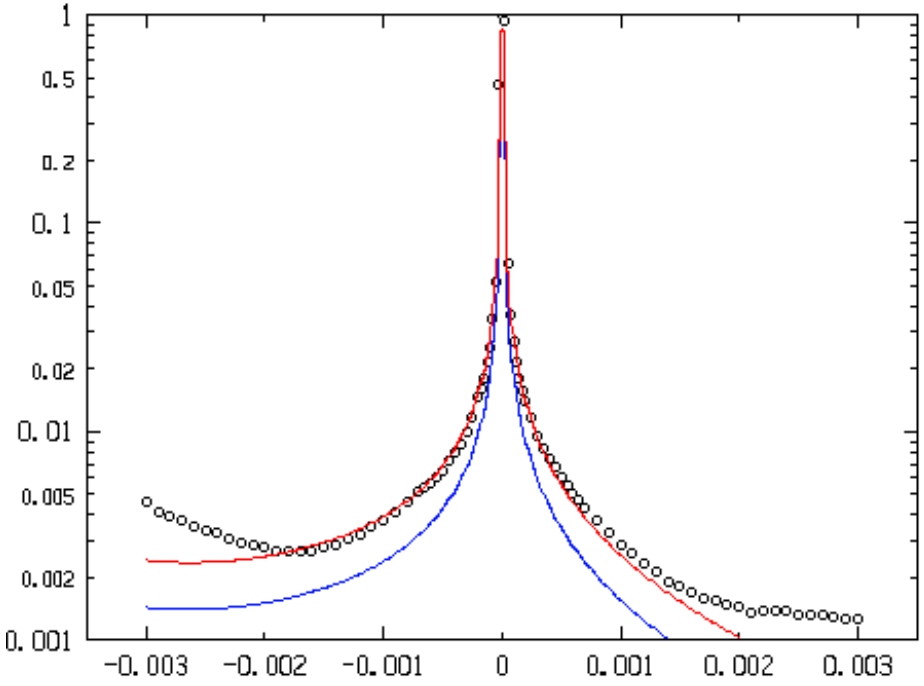
Contains information about the property and structure of the Au nanoparticle films? Are we able to fit this part by modifying our codes?

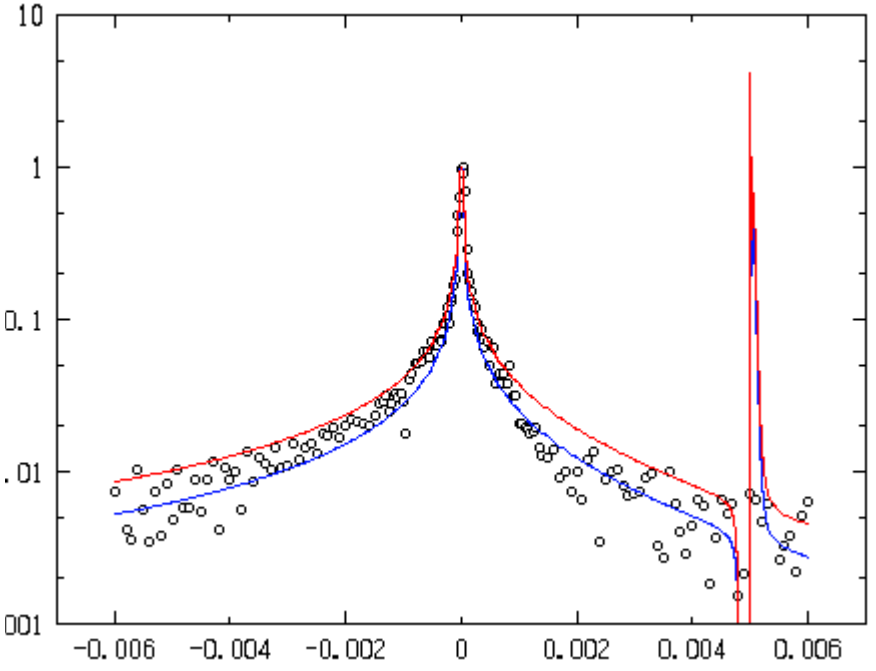
Due to the surface tension difference between water and solvent for nanoparticle?

Should we compare it to thin solvent material film on water surface?

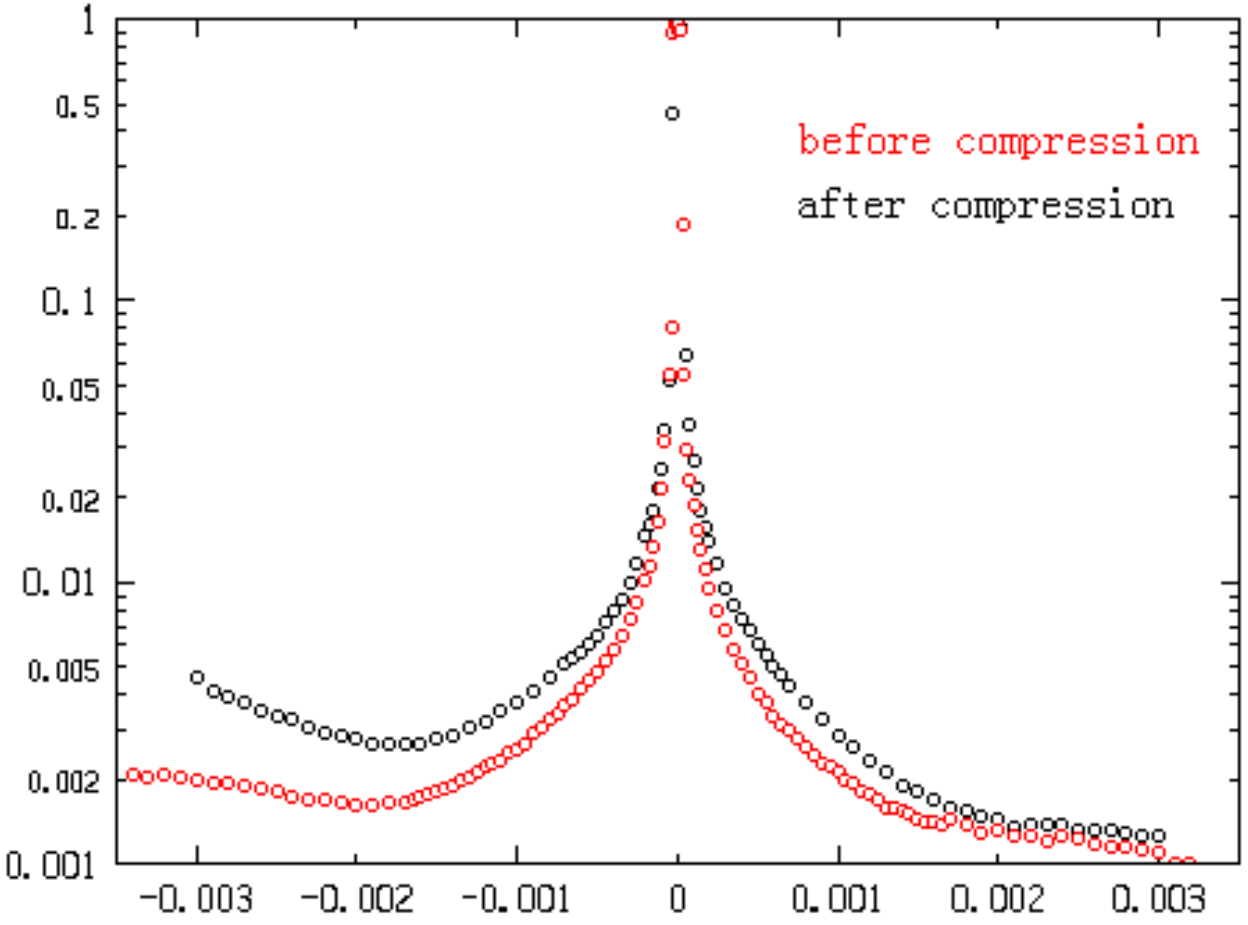
After compression
(compared to uncompressed results)

Au 331,Qz=0.22 ,
red-- fitted η =31 mN/m
blue-- uncompressed η =45 mN/m





Au 345 Qz=0.44 ,
red--fitted η =38 mN/m
blue—uncompressed η =48 mN/m



How does the compression lower surface tention of this system? Through increasing thickness of the solvent or increasing density of nanoparticles?

Surface tension of Heptane

ɣ (mN/m-1 ±0.02 mN/m-1)

n-alkane	*T*/K	this work	Jasper[3]
n-C_7H_{16}	293.15	20.53	20.28
	303.15	19.49	19.27
	313.15	18.50	18.25
	323.15	17.44	17.24
	333.15	16.50	16.22